Title

Exothermal Feeder Mass

Specification

Background

The invention relates to an exothermal feeder mass containing aluminum and magnesium, at least one oxidizing agent, a temperature-resistant SiO_2-containing filler, and an alkali silicate as the binder.

Prior Art

In exothermal feeder masses aluminum is used to cause an exothermal reaction with the oxidizing agent. Known feeder masses also contain a reactive fluorine compound which reacts with a passivating oxide skin on the aluminum powder so that the latter can react with the oxidizing agents.

One such feeder mass is described in DE-C-25 32 745. It contains among other materials, aluminum powder, an unspecified aluminum oxide and an organic material (phenol resin, urea resin or furan resin, starch) or an inorganic binder (silica sol, colloidal aluminum oxide) and an oxidizing agent for the fine-particle metal. The use of alkali silicates as binders is not mentioned. The fluorine compounds, called "fluoride catalysts", such as cryolite, fluorspar or sodium silicofluoride are important. The proportion of the fluorine compound can be 0.1 to 20% by weight. According to the examples the proportion of the fluoride compound is between 1.0 and 2.0%.

The presence of the fluorine compound in the exothermal feeder mass reduces the starting reaction temperature of the aluminum. This function results, for example, from the fact that for the likewise described heat-insulating feeder mass without aluminum the proportion of the fluoride compound can decrease to 0%.

DE-A-29 23 393 mentions among other material, exothermal feeder masses with aluminum power, cryolite, iron oxide, sand and aluminum oxide fibers. The latter should be preserved as fibers.

DE-C-28 31 505 describes an exothermal feeder mass with an Al_2O_3 additive which can be construed as an inert filler. Alkali silicates are not used, but the addition of a fluoride-containing flux (cryolite) is always necessary. Magnesium is not used.

DD-60 121 describes an exothermal feeder mass based on aluminum with the addition of water glass and a fluoride- containing flux. Aluminum oxide is not mentioned.

Since for environmental and process-engineering reasons there is a need for a fluoride-free exothermal feeder mass, it has already been suggested that an exothermal feeder mass without active fluorine portions be made available. One such feeder mass contains not only aluminum, but also magnesium or an aluminum-magnesium alloy. The passivity caused by the oxide skin on the aluminum is overcome by the temperature which occurs when the magnesium burns so that the aluminum also reacts with the oxidizing agent, by which a higher temperature is reached overall. In doing so, unwanted reactions occur in the feeder mass.

It was found that for fluoride-free exothermal feeder masses which contain aluminum and magnesium and also fillers with high SiO_2 content and alkali compounds (for example, from water glass) as the binder and alkali nitrates as the oxidizing agent, a so-called "hollow fire" is

formed which probably originates from vitrification of the SiO_2-containing fillers with the alkali compounds.

This hollow fire is evidenced by the formation of large cavities in the feeder wall which are connected by channels to the molten iron in the feeder. Iron losses occur due to penetration of the molten iron into these cavities. Moreover, this iron can only be separated from the reacted feeder mass with difficulty, so that it is almost impossible to re-process the iron.

The object of this invention is to reduce the so-called "hollow fire".

It has been found that surprisingly a hollow fire does not occur when a reactive or extremely finely ground aluminum oxide is added to the feeder mass.

Brief Description of the Drawings

Figure 1 is a cross-sectional view of a feeder composition showing a host of small cavities.

Figure 2 is a comparison feeder composition disclosing large cavity volumes which are connected with channels.

The subject matter of the invention is thus an exothermal feeder mass which contains about 2.5 to 20% by weight of a reactive aluminum oxide with a specific surface area of at least about 0.5 m^2/g and an average particle diameter (d_{50}) from about 0.5 to 15 microns and which is essentially free of fluoride-containing fluxes.

The reactive aluminum oxide generally contains up to about 5% OH groups. When the proportion of OH groups is relatively low, reactivity is also achieved by the very small size of the

aluminum oxide particles.

"Essentially free" is defined as having a fluoride content below 1.0, preferably below 0.5, most preferably below 0.1% by weight.

The exothermal feeder mass, as claimed in the invention after reaction, contains only small cavities which are not connected to one another by channels so that no iron from the feeder core can intrude.

It is believed that the reactive aluminum oxide reacts with the existing alkali compounds so that it can no longer react with the SiO_2-containing filler resulting in vitrification and cavity formation. When hollow fire no longer occurs, during and after the end of the reaction of the feeder mass, the strength of the mass also increases.

The reactive aluminum oxide in the feeder mass of the invention preferably has a specific surface area of about 1 to 10 m^2/g. Generally the composition of the feeder mass of the invention is as follows:

Aluminum:	20 - 35% by weight, preferably 20 - 23% by weight
Magnesium:	1.5 - 10% by weight, preferably 2 - 7% by weight
Oxidizing agent:	8 - 20% by weight, preferably 10 - 15% by weight
Reactive aluminum oxide:	4 - 18% by weight, preferably 8 - 13% by weight
Alkali silicate:	8 - 22% by weight, preferably 10 - 13% by weight or 17 - 23% by weight
SiO_2-containing filler:	58.5 - 17% by weight, preferably 43 - 29% by weight

The preferred amounts of the alkali silicate depend on the filler that is chosen. For fillers with a smaller bulk density (for example, hollow microspheres) the preferred amount of the alkali silicate is higher.

The oxidizing agent, as in conventional feeder masses, is iron oxide and/or an alkali nitrate, such as sodium or potassium nitrate, or the reduction product of the latter (alkali nitrite or alkali oxide) reacting with the reactive aluminum oxide.

Preferably the SiO_2-containing filler has a SiO_2 content of at least 50% by weight, preferably more than 60% by weight.

The temperature-resistant SiO_2-containing fillers can be quartz, sand and/or aluminum silicates, in the latter case preferably hollow microspheres, ground chamotte and/or mineral fibers being used.

The reactive aluminum oxide preferably has the following properties:

Al_2O_3 content	> 90%
Content of OH-groups:	up to 5% (depending on the particle diameter)
Specific surface area (BET)	about 1 to 10 m^2/g
Average particle diameter (d_{50}):	0.5 to 15 microns

The subject matter of the invention is also a process for reducing the hollow fire in essentially fluoride-free feeder masses. The process is characterized by a feeder mass as defined above being used.

It was furthermore found that when using the feeder mass of the invention, a change of the molten iron contained in the feeder mass, which change extends into the casting, surprisingly

occurs. The basic metallic structure is changed such that degeneration of the solidified casting mass due to the formation of lamellar graphite is prevented and the desired spheroidal graphite is formed. This can possibly be attributed to the presence of magnesium in the feeder mass as a spherogenic additive, although it does not come directly into contact with the molten iron and therefore no interaction between the two could be expected. A reaction of the magnesium contained in the feeder mass with the molten iron in the vapor phase is not likely, as magnesium has an extremely low vapor pressure and the feeder mass contains air inclusions between the grains of fine-grain mineral, so that the vaporous magnesium would immediately react with atmospheric oxygen. The effect which can be achieved by the invention is probably due to the feeder mass containing impurities (for example, sulfur) which can diffuse without the magnesium in the feeder mass into the molten iron and in this way can react with the very small amounts of the spherogenic additive (for example, magnesium) in the molten iron, so that when the iron solidifies, lamellar graphite rather than spheroidal graphite forms. It is assumed that the magnesium in the feeder mass reacts with the impurities contained therein so that they can no longer diffuse into the molten iron. The magnesium therefore apparently has a "scavenger" function.

In addition to the magnesium, other spherogenic additives, such as cerium, can be used. Alkali metals or alkaline earth metals other than magnesium, for example, calcium, are not as well suited since they easily oxidize in air.

The subject matter of the invention is thus also a process for preventing graphite degeneration in the feeder neck area and in the area which extends into the casting. This process is characterized by a feeder mass as defined above being used.

The invention is explained by the following examples.

Example 1

Formulation:

Aluminum (0.063 - 0.5 mm grain size)	20% by weight
Sodium nitrate as oxidizing agent:	15% by weight
Magnesium (0.1 - 0.5 mm grain size)	4.5% by weight
Reactive Al_2O_3: Al_2O_3 content 99%, BET surface < 6 m^2/g, d_{50} 4-8 microns	9% by weight
SiO_2 sand (0.1 - 0.5 mm grain size)	40.5% by weight
Water glass (43 - 45% solution)	11% by weight

The components were thoroughly mixed, and a feeder mold was filled with the resulting mass. The feeder mold was gassed with carbon dioxide. The water glass reacted with the carbon dioxide resulting in the formation of colloidal silicic acid and sodium carbonate which hardened the feeder mass. Then the mass was dried until the weight is constant.

The feeder was placed on the casting model and thus rammed up, whereupon molten iron was poured into the mold. In doing so the feeder mass ignited as the temperature rises, the sodium carbonate obtained from the water glass and the reaction product of the sodium nitrate preferably reacted with the reactive Al_2O_3 so that the hollow fire which occurred during the reaction with sand was reduced. After the end of the casting process the feeder was removed. After the reaction the feeder (1) showed in cross section a host of small cavities (2) which were

not interconnected by channels and thus which did not contain any iron either (Figure 1).

Example 2

Formulation:

Aluminum (as in example 1)	20% by weight
Sodium nitrate (as in example 1)	10% by weight
Magnesium (as in example 1)	4% by weight
Reactive Al_2O_3 (as in example 1)	12.5% by weight
SiO_2 hollow microspheres (0 - 0.5 mm grain size) bulk weight 350 cm^3/g, SiO_2 content 55-65%)	36.5% by weight
Water glass (as in example 1)	17% by weight

The components were mixed with one another as in example 1, placed in a feeder mold, gassed with carbon dioxide, and dried. Casting was also carried out as in example 1. The cross section of the reacted feeder mass showed essentially the same pore structure as the feeder from example 1.

Example 3 (comparison)

The formulation was the same as in example 1, but instead of reactive Al_2O_3, 9% by weight Al_2O_3 with the following properties were used: Al_2O_3 content 99%, grain size 0 to 0.5 mm (d_{50} = 200 microns).

Processing continued as in example 1. The resulting feeder (1) (see Figure 2 for an extract from the feeder wall) after the reaction showed a major hollow fire with a large cavity

volume in the center which was connected via channels to smaller cavities (2) which extended into the region of the molten iron. All the cavities were filled with solidified iron. When the feeder was crushed, residues of the reacted feeder mass adhered to the pieces of iron. The compressive strength of the conventionally produced cylindrical test piece (d = 50 mm, h = 50 mm) for quality control of the feeder mass from Example 3 was about 35% less than that of the test piece from Example 1.

Abstract

An exothermal feeder mass is described, containing aluminum and magnesium, at least one oxidizing agent, a SiO_2-containing filler, and an alkali silicate as the binder. It is characterized in that it contains about 2.5 to 20% by weight of a reactive aluminum oxide with a specific surface of at least about 0.5 m^2/g, an average particle diameter (d_{50}) from about 0.5 to 8 microns and is essentially free of fluoride-containing fluxes.